Photocatalytic degradation of sulfa drugs with TiO_2, Fe salts and $TiO_2/FeCl_3$ in aquatic environment—Kinetics and degradation pathway

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ABSTRACT

The photocatalytic degradation of sulfanilamide, sulfacetamide, sulfathiazole, sulfamethoxazole and sulfadiazine in aqueous solutions was examined during their irradiation with UV-A (366 nm) with TiO_2, Fe salts and $TiO_2/FeCl_3$ catalysts. The study was carried out by HPLC-UV, HPLC/MS-EI and total organic carbon (TOC) methods.

It was found that sulfonamides underwent photocatalytic degradation in the presence of TiO_2, $TiO_2/FeCl_3$ and Fe^{3+} salts, and the optimum catalyst for this process can be $FeCl_3$. Based on the identified intermediate products, a degradation pathway was proposed. Moreover, the rate of photocatalytic process carried out with $FeCl_3$ as well as the relationship between the pH of irradiated solutions, initial concentrations of sulfanilamide and $FeCl_3$ were stated.

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1. Introduction

Sulfonamides (sulfanilamide derivatives) are important bacteriostatic agents still commonly used in human and veterinary medicine. In the last decade, consumption of sulfonamides has decreased; however, in animal food production, they are still one of the most popular active antimicrobial agents. Sarmah et al. [1] have reported that in different countries, sulfonamides represent from 2% (USA) to 22% (UK, Kenya) of used veterinary antibiotics. The sulfonamides are excreted from the human body and animal organisms partially unmetabolised but also as the biotransformation products. The metabolites (glucoronide and N-4-acetylated sulfonamides) are converted back to the parent form in liquid manure [2]. The expired and unused drugs containing sulfonamides are also introduced into sewage from the households.

Moreover, sulfonamides and sulfonylurea compounds (e.g., asulam, chlorsulfuron, cinosulfuron, triasulfuron) are used as herbicides for agriculture. In the environment, they undergo decomposition into, among others, simpler sulfonamides.

Sulfonamides are polar, amphoteric substances that are readily soluble in water. [1,3]. For this reason, they possess high migration ability in the environment [4,5].

Due to the aforementioned facts, traces of sulfonamides are present in almost all surface waters [6–11]. The identified sources by which significant amounts of these compounds are introduced to groundwater and surface water are effluents from waste dumps [12], animal manure [1,3,13] and manure waste lagoons from swine farms [14], among others.

Capleton et al. [15] have been found that sulfonamides used in veterinary medicines are typically ejected directly into the aquatic environment, thus having a high potential to reach the environment, high toxicity and high 'Priority for Detailed Risk Assessment.' Similar conclusions were presented in other publications [3,11]. Moreover, the sulfonamides can be accumulated in various organisms of a food chain [1,6,8]. Although they are present in the environment at low levels, they may cause drug-resistance of pathogenic bacteria.

Sulfonamides show a semi-resistance to biological degradation [11,13,16–20]; thus, the biological methods used during sewage treatment seem to be ineffective. Available data in the literature have discrepancy in information concerning the possibility of removal of sulfonamides from wastewater during their biological treatment. Peng et al. [21] have reported that this process is practically 100% effective. Similarly, the authors of the Poseidon report have demonstrated that biological treatment processes guarantee very high removal by degradation of sulfamethoxazole in influent [11]. However, data published in the same report give evidence that the concentration of this sulfonamide in wastewater treatment plant (WWTP) influents can be lower than in effluents. Clara et al. [16] have reported that due to the low tendency of sulfonamides to accumulate in sludge, removal rates between 50 and 60% were achieved. On the other hand, Ternes et al. [4] have

stated that removal of sulfamethoxazole in the effluent of Braunschweig WWTP was only 24%.

The photocatalytic process method results in effective degradation of pollutants regardless of their biological stability and toxicity. This process relies on the oxidation of organic compounds with the participation of hydroxyl radicals ($HO^\bullet$), which are generated as a result of illumination by radiation at $\lambda < 400$ nm and the suspension of particles of heterogeneous catalyst, e.g., TiO_2 [22]:

$$TiO_2(aq) + h\nu \rightarrow TiO_2(h_{VB}^+, e_{CB}^-)(aq) + O_2 \rightarrow HO^\bullet + O_2^{\bullet-} + H^+$$
(1)
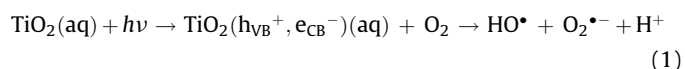
or in the presence of homogeneous catalysts, e.g., Fe^{3+} salts [23]:

$$Fe^{3+}(aq) + h\nu \rightarrow Fe^{2+}(aq) + HO^\bullet + H^+$$
(2)
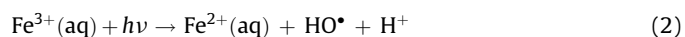
Moreover, $HO^\bullet$ radicals can be produced by Fe^{2+} salts from H_2O_2 by the photo-Fenton process [24]:

$$Fe^{2+}(aq) + H_2O_2 + H^+ + h\nu \rightarrow Fe^{3+}(aq) + HO^\bullet$$
(3)
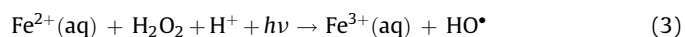
In the course of our previous studies, it was confirmed that sulfonamides are susceptible to photocatalytic degradation in the presence of TiO_2 [17]. Similar results were also presented in researches of others authors [18,25–29]. Maurino et al. [25], Vulliet et al. [26] and Rafqah et al. [27] have determined the kinetics and chemical mechanism of sulfonylurea herbicide photocatalytic transformation. Kaniou et al. [28] have investigated the kinetics and optimisation of photocatalytic degradation of sulfamethazine in aqueous heterogeneous solutions containing anatase, P-25 or ZnO. Hu et al. [29] have examined the kinetics and degradation pathway of sulfamethoxazole and related antimicrobial agents in the presence of different commercial photocatalysts. In turn, Abellan et al. [18], besides the kinetics and reaction pathway, have also examined the biodegradability of the products of photocatalytic degradation of sulfamethoxazole.

The aforementioned examples involve heterogeneous catalysis. However, the photocatalytic process may also be performed under homogeneous conditions. In this case, Fe^{3+} salts are the most frequently used photocatalyst. In the literature, the course and mechanism of degradation of sulfanilamide and its derivative (asulam), occurring during the photochemical reaction initiated by the $[Fe(OH)(H_2O)_5]^{2+}$ ion, has been described [30].

The possibility of sulfonamide degradation by photo-Fenton [20] and in the presence of TiO_2-anatase/$FeCl_3$ mixture was also studied [31].

The reaction mechanism and sulfonamide degradation pathway in the presence of photocatalyst containing Fe salts, namely, TiO_2/$FeCl_3$, has not been presented to date. The aims of our work were the comparison of: (i) the course and mechanism of photodegradation of selected sulfonamides, (ii) the efficiency of photocatalytic degradation and (iii) the mineralisation of sulfonamides in aqueous solutions during their irradiation with UV-A in the presence of TiO_2, $FeCl_3$ and TiO_2-anatase/$FeCl_3$ as catalysts. It was also intended to determine the effect of pH and initial concentrations of reagents (with optimal catalyst only) on the rate of the photocatalytic process.

2. Materials and methods

2.1. Reagents

The characteristics of investigated sulfonamides are presented in Table 1.

All chemicals used throughout this study were of analytical grade, and their solutions were prepared in distilled water. Two types of titanium(IV) dioxide were used as received. TiO_2-P25 was obtained from Degussa AG (anatase/rutile 80:20, a mean BET surface area of 43 $m^2\,g^{-1}$, an average particles size of 21 nm) and TiO_2-RH powder, from Riedel de Haën (anatase 100%, a mean BET surface area of 9–11 $m^2\,g^{-1}$, residues on filter >40 μm after dispersion in water $<0.02\%$). The iron(III) chloride ($FeCl_3$), iron(III) nitrate ($Fe(NO_3)_3$), iron(III) sulfate ($Fe_2(SO_4)_3$) and iron(II) sulfate ($FeSO_4$) used as catalysts were obtained from POCH, and iron(II) chloride ($FeCl_2$) was obtained from Merck.

Solid TiO_2 (2.5 g L^{-1}) or Fe salt stock solution was added to solutions of selected sulfonamides in distilled water (0.1 mmol L^{-1}). Moreover, a mixture of TiO_2-RH (2.5 g L^{-1}) and $FeCl_3$ was added to these solutions. The end concentrations of Fe^{2+} or Fe^{3+} ions in samples were 1.0 mmol L^{-1} (with the exception of the experiment described in Section 3.7). In experiments involving the effect of the initial concentration of sulfonamide and $FeCl_3$ on the initial reaction rate, their concentrations were in the range of 0.01–1.0 and 0.1–1.5 mmol L^{-1}, respectively. Before illumination, the samples were homogenised for 10 min by means of magnetic stirrers.

2.2. Irradiation

In all experiments, five open glass crystallisers (volume: 500 cm^3, exposed surface: 102 cm^2) containing 100 cm^3 of samples were irradiated by four UV lamps (Philips TL-40 W/ 05 at λ_{max} 366 nm). The intensity of UV-A radiation, determined by Parker's actinometer [32], was 2.9 mW cm^{-2}. During the entire experiment, mixtures were magnetically stirred and had free contact with air. The temperature of samples was 21 ± 2 °C. In all cases, no buffer was added to sulfonamide solutions. Only in the experiment described in Section 3.5, the pH of the irradiated samples was adjusted with concentrated HCl or NaOH solutions (<1 mL). In other experiments, samples at natural pH (without correction) were used, and this value was maintained during all experimental runs.

2.3. Analytical methodology

After the appropriate irradiation time samples were centrifuged (30 min, 4000 RPM). Before and after irradiation, the concentration of sulfonamides in mixtures was determined using HPLC (column Supelcosil Suplex pKB-100 LC-18 5 μm, 250 mm × 4.6 mm, detectors Merck UV L-L 7400 or Waters TAD 486, $\lambda = 254$ nm) and mobile phases K_2HPO_4 (pH 8.9)/CH_3CN in the ratio 92:8 (for SN and SA) and [$HCOONH_4$/$HCOOH$ (pH 4.0)]/CH_3CN in the ratio 1:1 (for SD, SMX and ST).

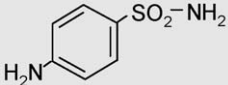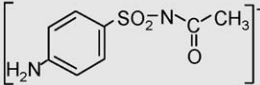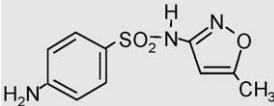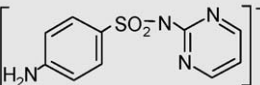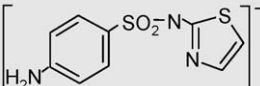Total organic carbon (TOC) was measured by Total Carbon Analyser SHIMADZU 5000A. The colorimetric determination of Fe^{2+} concentration with 1,10-phenantroline was done following the ISO 6332 method. The concentration of Fe^{3+} in irradiated samples was calculated as a difference between the initial concentration of Fe-ions, added as the photocatalyst, and Fe^{2+} concentration. The pH and concentration of oxygen dissolved in illuminated samples were measured by multimeter HD22569.2 (Delta OHM).

2.4. Identification of the intermediate photoproducts

The samples irradiated for 60 and 120 min were analysed by HPLC–MS/EI using detectors Waters PDA 996, Waters TMD and column Supelcosil Suplex pKB-100 LC-18 (5 μm, 250 mm × 4.6 mm), with the mobile phase H_2O/CH_3CN, 95:5 and 1:1. The results of analysis of sulfonamides were confirmed with the use of standards.

Table 1
The characteristics of investigated sulfonamides and the results of photocatalytic processes.

Sulfonamides/manufactured/structure	Abbr. in text	pKa_1[a]	pKa_2[a]	Photocatalyst	pH	k (min^{-1}) or (L mmol^{-1} min^{-1})	Irradiation range[b] (min)	r_o (mmol L^{-1} min^{-1})	Degradation[c] (%)	Decrease of TOC[d] (%)
Sulfanilamide/POCH	SN	2.40	10.43	TiO$_2$-P25	6.18	0.0391	0–90	0.00391	55	97
				TiO$_2$-RH	6.69	0.0312	0–90	0.00312	50	83
				TiO$_2$-RH/FeCl$_3$	3.08	1.44[e]	0–45	0.0144[e]	74	23
				FeCl$_3$	3.05	0.0677	0–30	0.00677	83	58
Sulfacetamide natrium salt/POCH	SA	1.78	5.38	TiO$_2$-P25	6.50	0.0388	0–90	0.00388	46	<90
				TiO$_2$-RH	7.35	0.0133	0–90	0.00133	24	65
				TiO$_2$-RH/FeCl$_3$	3.03	0.229[e]	0–90	0.00229[e]	38	30
				FeCl$_3$	3.09	0.0443	0–20	0.00443	59	27
Sulfamethoxazole/Sigma	SMX	1.60	5.81	TiO$_2$-P25	4.50	0.0318	0–90	0.00318	46	≈90
				TiO$_2$-RH	5.63	0.0241	0–90	0.00241	39	63
				TiO$_2$-RH/FeCl$_3$	2.98	0.439[e]	0–45	0.00439[e]	48	20
				FeCl$_3$	3.03	0.0484	0–30	0.00484	64	43
Sulfadiazine natrium salt/Sigma	SD	2.00	6.48	TiO$_2$-P25	6.02	0.0406	0–90	0.00406	52	–
				TiO$_2$-RH	6.60	0.0128	0–90	0.00128	25	22
				TiO$_2$-RH/FeCl$_3$	2.95	0.886[e]	0–30	0.00886[e]	65	7
				FeCl$_3$	2.91	0.0298	0–45	0.00298	48	10
Sulfathiazole natrium salt/Sigma	ST	2.36	7.23	TiO$_2$-P25	6.31	0.0400	0–90	0.00400	52	<90
				TiO$_2$-RH	7.10	0.0181	0–90	0.00181	28	64
				TiO$_2$-RH/FeCl$_3$	3.11	1.79[e]	0–90	0.0179[e]	92	13
				FeCl$_3$	3.15	0.0515	0–30	0.00515	66	4

[a] $SH_2^+ \overset{Ka_1}{\longleftrightarrow} SH \overset{Ka_2}{\longleftrightarrow} S^-$.
[b] The k values were estimated based on these irradiation ranges.
[c] Of sulfonamides after irradiation for 20 min.
[d] After irradiation for 300 min.
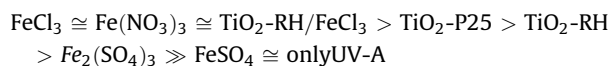[e] Fitting to the second-order reaction rate.

3. Results and discussions

3.1. The comparison of photocatalytic activities of selected catalysts (Fe salts, TiO$_2$ and TiO$_2$-RH/FeCl$_3$)

The dynamics of photocatalytic degradation of SN (0.1 mmol L^{-1}) in the presence of selected catalysts Fe salts (1.0 mmol L^{-1}), TiO$_2$-RH/FeCl$_3$ (2.5 g L^{-1}/1.0 mmol L^{-1}), TiO$_2$-P25 (2.5 g L^{-1}) and TiO$_2$-RH (2.5 g L^{-1}) are presented in Fig. 1. The samples were illuminated by the UV-A radiation. The natural pH of samples containing Fe^{3+} salts (with and without TiO$_2$-RH), Fe^{2+} salts, TiO$_2$-P25 and TiO$_2$-RH were about 3, about 4, 6.18 and 6.69, respectively (Table 1).

During the first 20 min of irradiation, the highest degradation rate of SN was observed in samples containing TiO$_2$-RH/FeCl$_3$, FeCl$_3$ and Fe(NO$_3$)$_3$. However, during longer irradiation times (up to 20 min) a significant slowing down of reactions carried out with the above-mentioned catalysts was observed. A similar slowing down was not observed in samples containing TiO$_2$-P25 and TiO$_2$-RH. For this reason, in the presence of TiO$_2$-RH/FeCl$_3$, FeCl$_3$, Fe(NO$_3$)$_3$, TiO$_2$-P25 and TiO$_2$-RH after about 60 min of irradiation, the degradation levels of SN were similar (>80%). In the case of Fe$_2$(SO$_4$)$_3$, the photocatalytic degradation of SN occurred at a significantly lower rate (Fig. 1). The photocatalytic activity of Fe^{2+} salts was negligible. The SN degradation in samples at natural pH (about 4) containing FeSO$_4$ or FeCl$_2$ (data not showed in Fig. 1) was

similar and was below 3% and about 30% after 20 and 300 min of irradiation, respectively. On the other hand, after correction of pH (to 3.07) of samples containing SN with FeSO$_4$ or FeCl$_2$ and after their irradiation, the degradation degree of SN was 11 and 67%, respectively. However, these values were still lower than those obtained for the other investigated catalysts (Table 1). Based on comparisons of the degradation degree after 20 min of irradiation of samples (Fig. 1, Table 1), the following series of catalyst activity was found:
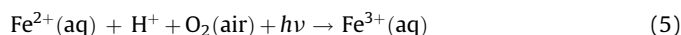
FeCl$_3$ ≅ Fe(NO$_3$)$_3$ ≅ TiO$_2$-RH/FeCl$_3$ > TiO$_2$-P25 > TiO$_2$-RH
> *Fe$_2$(SO$_4$)$_3$* ≫ FeSO$_4$ ≅ onlyUV-A

The initiation step of the photocatalytic process carried out in the presence of TiO$_2$ and Fe^{3+} salts depends on the generation of hydroxyl radicals (Eqs. (1) and (2)). This fact is confirmed by results described in Section 3.2.

A low activity of Fe^{2+} salts was consistent with the assumption that in photocatalytic processes, Fe^{2+} ions are acceptors of free hydroxyl radicals [23,30]:

$$Fe^{2+}(aq) + HO^\bullet + H^+ \rightarrow Fe^{3+}(aq) \tag{4}$$
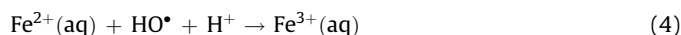
In the case of Fe^{2+} salts, the photocatalytic process was most probably initiated by Fe^{3+}ions. These ions can be the product of Fe^{2+} ions oxidation, according to the following scheme:

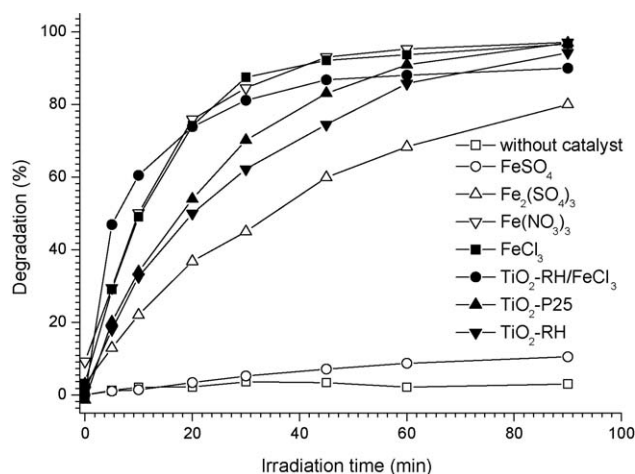$$Fe^{2+}(aq) + H^+ + O_2(air) + h\nu \rightarrow Fe^{3+}(aq) \tag{5}$$

Fig. 1. The degradation of SN (0.1 mmol L^{-1}) at natural pH, during UV-A irradiation without catalyst and in the presence of FeSO$_4$ (1.0 mmol L^{-1}), Fe$_2$(SO$_4$)$_3$ (0.5 mmol L^{-1}), Fe(NO$_3$)$_3$ (1.0 mmol L^{-1}), FeCl$_3$ (1.0 mmol L^{-1}), TiO$_2$-RH/FeCl$_3$ (2.5 g L^{-1}/1.0 mmol L^{-1}), TiO$_2$-P25 (2.5 g L^{-1}) or TiO$_2$-RH (2.5 g L^{-1}).

Fig. 2. The change of Fe^{2+} concentration (A) and ln C/C_o of Fe^{3+} concentration (B) in solution of SN (0.1 mmol L^{-1}) during UV irradiation with FeCl$_3$ (1.0 mmol L^{-1}) or TiO$_2$-RH/FeCl$_3$ (2.5 g L^{-1}/1.0 mmol L^{-1}).

The photocatalytic degradation of organic compounds can be inhibited by inorganic ions (sulfates, phosphates, etc.) in varying degree and depending on their concentration. The inhibitory effect can be attributed to a decrease of the rate of generation of HO$^•$ radicals due to the formation of less reactive inorganic radicals (e.g., SO$_4^{•-}$). Moreover, this effect can be explained by the formation of less photoreactive Fe^{3+} complexes with anions (FeSO$_4^+$) [33]. The complexation reactions result in a decrease of hydrated Fe^{3+} ions in irradiated solutions. This effect is particularly clear for SO$_4^{2-}$ ions. According to Wu and Deng [23], the photocatalytic activity of Fe(NO$_3$)$_3$ is higher than of FeCl$_3$; however, this fact was not confirmed by the results of our experiments. Having the highest activity among these salts, FeCl$_3$ was used as optimum photocatalyst for the rest of the experimental runs. It is cheaper and, above all, safer for the environment (non-biogenic properties of chlorides as distinct from nitrate ions).

3.2. Confirmation of HO$^•$ radical involvement in photocatalytic reactions

In order to confirm the presence of HO$^•$ as the main oxidising agent, photocatalytic hydroxylation of benzene (1 mmol L^{-1}) was carried out [34]. In all samples containing investigated photocatalysts, namely, FeCl$_3$ (1.0 mmol L^{-1}), TiO$_2$-RH/FeCl$_3$ (2.5 g L^{-1}/1.0 mmol L^{-1}), TiO$_2$-P25 (2.5 g L^{-1}) and TiO$_2$-RH (2.5 g L^{-1}), the formation of phenol was observed. Its maximum concentration was recorded after 4–7 min of irradiation to be 26.4, 12.5, 8.6 and 4.5 μmol L^{-1} for FeCl$_3$, TiO$_2$-P25, TiO$_2$-RH and TiO$_2$-RH/FeCl$_3$, respectively. In the experiment, natural pH values of samples were used. According to Liu and Deng [34], this result can be evidence of the presence of hydroxyl radicals in photocatalytic reactions.

3.3. The dynamics of Fe^{3+} ion reduction

The reduction rate of Fe^{3+} to Fe^{2+} was estimated in solutions containing FeCl$_3$, with or without TiO$_2$. Fig. 2A shows the changes in Fe^{2+} concentration and Fig. 2B shows the changes in ln C(Fe^{3+}) during irradiation of SN solutions (0.1 mmol L^{-1}) with FeCl$_3$ (1.0 mmol L^{-1}) or TiO$_2$-RH/FeCl$_3$ (2.5 g L^{-1}/1.0 mmol L^{-1}).

It can be seen that Fe^{2+} concentration increased practically to a value equal the initial Fe^{3+} concentration (Fig. 2A). A linear correlation was found between ln C/C_o of Fe^{3+} ions and the irradiation time (Fig. 2B), which means that in both investigated
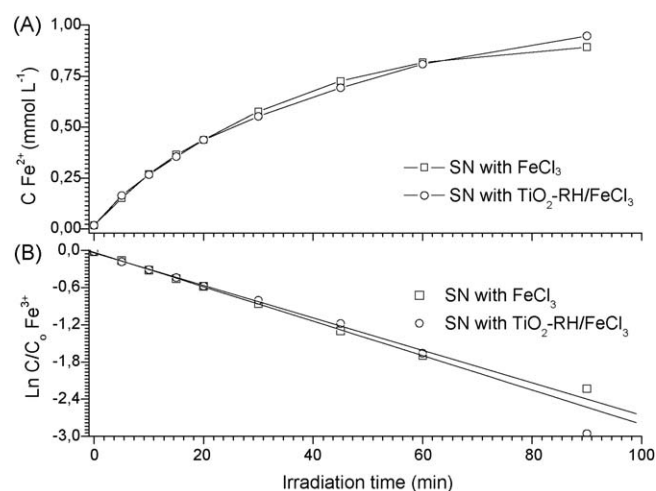
cases, the Fe^{3+} reduction was a pseudo first-order process. The reduction rate of Fe^{3+} was similar for FeCl$_3$ and TiO$_2$-RH/FeCl$_3$. For this reason, the participation of Fe^{3+} ions in degradation processes with FeCl$_3$ and TiO$_2$-RH/FeCl$_3$ was probably the same.

3.4. Measurement of the degree of aeration in investigated samples

The concentration of dissolved oxygen (O$_{2\,sol}$) was determined in SN solutions (0.1 mmol L^{-1}) containing FeCl$_3$ (1.0 mmol L^{-1}), TiO$_2$-RH/FeCl$_3$ (2.5 g L^{-1}/1.0 mmol L^{-1}), TiO$_2$-P25 (2.5 g L^{-1}) or TiO$_2$-RH (2.5 g L^{-1}). All samples were irradiated over a period of 0–90 min. In all analysed cases, the O$_{2\,sol}$ concentration decreased by about 5–10% over 0–30 min of irradiation and did not undergo a significant change during longer illumination (up to 30 min). The lowest concentration of O$_{2\,sol}$ (89%) was observed in samples containing TiO$_2$-RH/FeCl$_3$. The results may indicate that aeration of the investigated samples was sufficient. From this fact, it is clear that the rate of oxygen dissolved in irradiated samples is not a limiting factor the photocatalytic process rate under the experimental conditions.

3.5. Comparison of activities of selected photocatalysts at different pH

The activities of selected catalysts, FeCl$_3$ (1.0 mmol L^{-1}), TiO$_2$-RH/FeCl$_3$ (2.5 g L^{-1}/1.0 mmol L^{-1}), TiO$_2$-P25 (2.5 g L^{-1}) and TiO$_2$-RH (2.5 g L^{-1}), were compared at different initial pH in the range of 2–12 (pH correction – Section 2.2). Fig. 3 shows the determined relationships based on the degradation level of SN (0.1 mmol L^{-1}) after 20 min of UV-A irradiation.

A high degradation level was obtained after irradiation of samples in the presence of TiO$_2$-P25 over the entire investigated pH range. This catalyst showed the maximum activity in basic medium (SN degradation at pH 10.3 after 20 min of irradiation was 76%). At pH in the range of 3.5–4, the best catalyst was TiO$_2$-RH (max. 62% at pH 3.7). During irradiation of samples containing FeCl$_3$, the degradation of SN was observed only in a narrow pH range, and its maximum value (83%) was at about pH 3. The photocatalytic activity of Fe^{3+}(aq) ions is mainly connected with the products of their partial hydrolysis, namely with Fe(OH)$^{2+}$ ions [35]. The maximum concentration of these ions was found in solutions at pH 2.5–4 [23]. For this reason, Eq. (2) can be presented in another form:
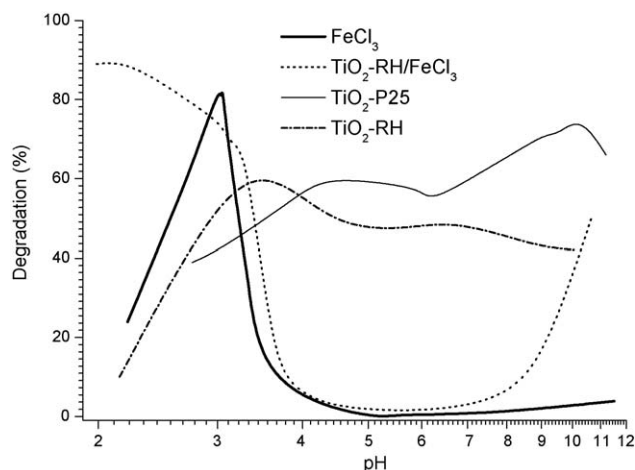
$$Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+} + HO^• \qquad (6)$$

Fig. 3. Effect of pH on the photocatalytic degradation of SN (0.1 mmol L^{-1}) with FeCl$_3$ (1.0 mmol L^{-1}), TiO$_2$-RH/FeCl$_3$ (2.5 g L^{-1}/1.0 mmol L^{-1}), TiO$_2$-P25 (2.5 g L^{-1}), or TiO$_2$-RH (2.5 g L^{-1}).

It is very important that the aforementioned pH values correspond to the natural pH values of FeCl$_3$ solution at concentrations about 1 mmol L^{-1}. The highest degradation level of SN was observed in samples containing TiO$_2$-RH/FeCl$_3$ (max. 90% at pH 2.2). However, this very low pH value decreases the possibility of practical use of this photocatalyst. The decrease of TiO$_2$-RH/FeCl$_3$ photoactivity in the pH range of 4–9 may be caused by a strong coagulation of catalyst.

3.6. Kinetics

In the opinion of a significant majority of researchers, the photocatalytic processes carried out in the presence of TiO$_2$ or FeCl$_3$ are pseudo first-order reactions [17,18,22,23,26,28,29,35]:

$$r = -\frac{dC}{dt} = kC \tag{7}$$

where r is reaction rate and k is the reaction rate constant.

For this reason, in order to estimate the kinetics of degradation processes in the presence of TiO$_2$ or FeCl$_3$, the following relationship was analysed:

$$\ln \frac{C}{C_o} = -kt \tag{8}$$

It is possible that SN degradation in the presence of TiO$_2$-RH/FeCl$_3$ (Fig. 1) is a pseudo second-order reaction and proceeds according to the following equation:

$$r = -\frac{dC}{dt} = kC^2 \tag{9}$$

In this case, a linear equation has the form:

$$\frac{1}{C} = kt + b \tag{10}$$

In order to determine the kinetics of each photocatalytic process, the samples of SN (0.1 mmol L^{-1}) containing FeCl$_3$ (1.0 mmol L^{-1}), TiO$_2$-RH/FeCl$_3$ (2.5 g L^{-1}/1.0 mmol L^{-1}), TiO$_2$-P25 (2.5 g L^{-1}) and TiO$_2$-RH (2.5 g L^{-1}) were irradiated. A linear relationship 1/C of SN versus irradiation time was established (Fig. 4A) based on the results obtained for reactions conducted with TiO$_2$-RH/FeCl$_3$. In the cases of TiO$_2$-RH, TiO$_2$-P25 and FeCl$_3$, the courses of changes in ln C/C_o of SN versus irradiation time were also fixed (Fig. 4B). Continuous lines illustrate second-order processes (Fig. 4A) and first-order processes (Fig. 4B). Dashed lines illustrate observed departure from the theoretical course of
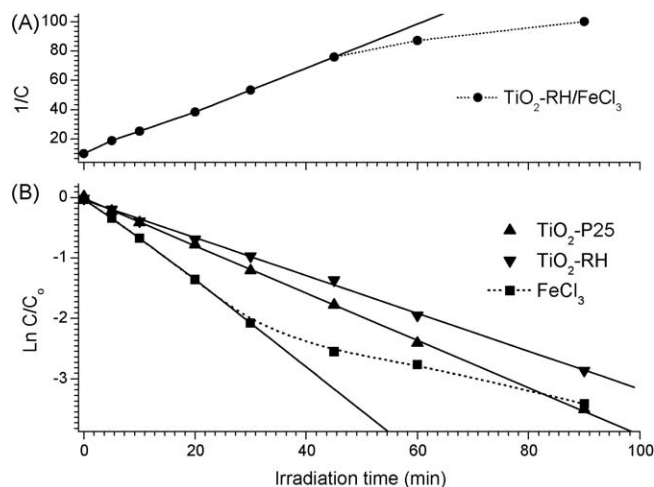

Fig. 4. Reaction order analysis for the photocatalytic degradation of SN (0.1 mmol L^{-1}) with: (A) TiO$_2$-RH/FeCl$_3$ (2.5 g L^{-1}/1.0 mmol L^{-1}); (B) TiO$_2$-P25 (2.5 g L^{-1}), TiO$_2$-RH (2.5 g L^{-1}), FeCl$_3$ (1.0 mmol L^{-1}). Solid line—the course of function for the second (A) or first (B) order reactions, dashed lines—differences in the plot for the experimental data.

function (8) or (10) for reactions conducted in the presence of Fe^{3+} salts (with and without TiO$_2$-RH).

During 0–45 min irradiation of samples containing TiO$_2$-RH/FeCl$_3$, an inverse of SN concentration was linearly dependent on irradiation time (Fig. 4A), and a pseudo second-order reaction rate law was observed.

In all analysed time intervals (0–90 min), the photocatalytic degradation of SN carried out with TiO$_2$-P25 and TiO$_2$-RH was a pseudo first-order reaction (Fig. 4B). In turn, the degradation process of SN in the presence of FeCl$_3$ was recognised as a first-order reaction, but only during 0–30 min irradiation. However, after longer irradiation time (up to 30 min), a considerable decrease was observed in the reaction rate (Fig. 4B, dashed line). Most probably, this fact is connected with the reduction of Fe^{3+} to Fe^{2+}, occurring in parallel during irradiation of samples (Fig. 2). Moreover, a decrease in the reaction rate may be caused by the competitive reaction of Fe^{2+} with free HO$^{\bullet}$ radicals (Eq. (4)). Based on experimental results (described in Section 3.7), we stated that a change in FeCl$_3$ concentration in the range from 0.7 to 1.5 mmol L^{-1} had practically no influence on the photocatalytic reaction rate. In turn, the decrease in the initial FeCl$_3$ concentration below 0.7 mmol L^{-1} caused a considerable decrease in its rate and may cause a change in the reaction order. Additionally, it is not excluded that the slowdown of the process may be caused by other competitive reactions with the participation of intermediates of SN degradation, including the formation of complexes with Fe^{3+}.

According to Mestankova et al. [36], in the cases of reactions catalysed by TiO$_2$-RH/FeCl$_3$, the Fe^{3+} ions can be acceptors of photoexcited electrons of TiO$_2$ surface:

$$e_{CB}^- + Fe^{3+} \rightarrow Fe^{2+} \tag{11}$$

The slowdown of the reaction cannot be explained by changes in pH during irradiation of samples. It was stated that during irradiation of SN solution (0.1 mmol L^{-1}) with FeCl$_3$ (1.0 mmol L^{-1}) for 90 min, the natural pH values decreased by less than 0.1.

The presented data (Fig. 2) show that oxidation of Fe^{2+} to Fe^{3+} (regeneration of catalyst, Eq. (5)) proceeds under experimental conditions at a low rate. As mentioned by Sun and Pignatello [37] and Mailhot et al. [38], oxygen molecules play an important role in the iron-photoassisted processes, including regeneration of Fe^{2+}. Catastini et al. [30] have proposed a scheme of reoxidation of Fe^{2+}

to Fe^{3+} conducted in acidic medium:

$$Fe^{2+} + O_2^{\bullet-} + 2H^+ \rightarrow Fe^{3+} + 2H_2O_2 \tag{12}$$
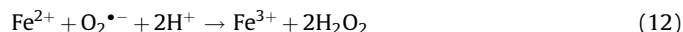
Formed H_2O_2 molecules can participate in Fenton or Fenton-like reactions (Eq. (3)) and ameliorate the efficiency of photocatalytic degradation of sulfonamides. On the other hand, Andreozzi and Marotta [39], studying photocatalytic degradation of benzoic acid in the presence of Fe^{3+}, noted that aeration has no effect on the photocatalytic reaction rate.

A high concentration of $O_{2\ sol}$ in samples was observed during the entire experiment. From this fact, it is clear that more intensive aeration does not cause an increase in the efficiency of photocatalytic reaction. The search for other methods of intensification of Fe^{2+} reoxidation will be the subject of further laboratory tests.

Based on results corresponding to kinetic equations (8) or (10), the k values were determined from Fig. 4 as slopes of the straight lines. The results of SN degradation in the presence of TiO_2-P25, TiO_2-RH, TiO_2-RH/$FeCl_3$ and $FeCl_3$ after 0–90, 0–90, 0–45 and 0–30 min of irradiation, respectively, were taken into consideration. The initial reactions rates r_o (Table 1) were calculated based on the determined k values. In the cases of processes carried out in the presence of $FeCl_3$, TiO_2-P25 and TiO_2-RH, the r_o values were calculated using the formula:

$$r_o = kC_o \tag{13}$$

and for processes with TiO_2-RH/$FeCl_3$, using the formula:

$$r_o = kC_o^2 \tag{14}$$

3.7. The effect of the initial concentration of substrates

The effect of the initial concentration of SN on its initial degradation rate and the Fe^{2+} formation during UV-A illumination was investigated. In these experiments, the initial concentration of $FeCl_3$ was 1.0 mmol L^{-1} and pH about 3. The results are shown in Fig. 5A.

Initially, an increase in the initial SN concentration (0.01–0.35 mmol L^{-1}) caused an increase in the degradation rate of SN as well as in the Fe^{2+} formation to the achievement of maximum values (Fig. 5A). This effect, caused by the increase in concentration of SN, may result from an increase in the reaction rate (Eq. (15))

and the simultaneous slowdown of a competing reaction (Eq. (5)).

$$SN + HO^{\bullet} \rightarrow oxidation products \tag{15}$$

Since the process of Fe^{2+} formation reflects the rate of generation of $HO^{\bullet}$ radicals, the concentration of SN also has an influence on this step. Further increase in the initial concentration of SN (0.35–1.0 mmol L^{-1}) induced a decrease in the degradation rate of sulfonamide and, to a lesser degree, a decrease in the rate of Fe^{2+} formation. The negative effect may depend on a decrease in the effective radiation flux due to adsorption of part of the radiation by SN. Additionally, it cannot be excluded that the increase in the concentration of SN can cause a decrease in $Fe(OH)^{2+}$ ions. Although the obtained experimental results did not confirm this hypothesis, there is a possibility of the formation of non-stable, complex compounds between SN and Fe^{3+}, negatively influencing $Fe(OH)^{2+}$ formation. On the other hand, according to the free-radical theory, a negligible change in the rate-limiting step (initiation) can cause significant changes in the rate of the entire free-radical process.

The effect of the initial concentration of $FeCl_3$ on the initial degradation rate of SN (0.1 mmol L^{-1}) during UV-A illumination is shown in Fig. 5B. Since the photochemical reaction is the rate-limiting step of SN degradation, an increase in its rate should be proportional to the radiant flux absorbed by $Fe(OH)^{2+}$ ions. For this reason, the increase in the concentration of these species, causing an increase in radiation absorption, should result in an increase in the reaction rate. Transmittance of the irradiated solutions containing SN and $FeCl_3$ at concentrations in the range of 0.1–0.7 mmol L^{-1} decreased by 50% (for $\lambda = 366$ nm). In turn, when the initial $FeCl_3$ concentration increased in the range from 0.8 to 1.5 mmol L^{-1}, transmittance decreased by only 20%, and the change in the r_o value was negligible (Fig. 5B). We suppose that this phenomenon is caused by the nearly complete use of the radiant flux by the irradiated solution. In this case, in order to enhance the reaction rate, the radiant flux should be increased. The occurrence of the aforementioned plateau is also connected with the thickness of the layer of illuminated solution.

3.8. Photocatalytic degradation of selected sulfonamides

Under established experimental conditions, none of the investigated sulfonamides underwent photolysis to a considerable level.
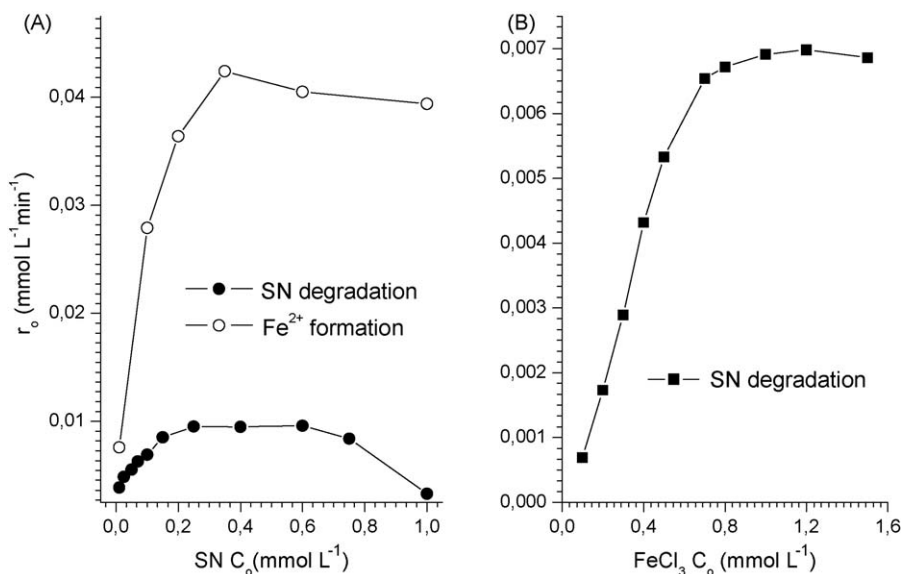

Fig. 5. Influence of the initial concentration of SN (A) on the initial rate of SN degradation or Fe^{2+} formation in the presence of $FeCl_3$ (1.0 mmol L^{-1}) and influence of the initial concentration of $FeCl_3$ (B) on the initial rate of SN (0.1 mmol L^{-1}) degradation in the presence of $FeCl_3$.

In fact, previously, the photolysis of SMX, ST [18,40] and SA [41,42] was described, but it was carried out under different conditions than those used in our studies. The cited studies concerned researches carried out with the use of atomic oxygen, free HO• radicals, a photosensitiser ("rose bengal") or UV radiation at a greater energy.

It was found that all investigated sulfonamides (SA, SD, SMX and ST) underwent photocatalytic degradation. The sulfonamide solutions (0.1 mmol L^{-1}) were irradiated with FeCl$_3$ (1.0 mmol L^{-1}), TiO$_2$-RH/FeCl$_3$ (2.5 g L^{-1}/1.0 mmol L^{-1}), TiO$_2$-P25 (2.5 g L^{-1}) and TiO$_2$-RH (2.5 g L^{-1}) at the natural pH value. The pH of samples and results obtained during experiments are presented in Table 1. The r_o values were calculated in a similar manner as in the case of SN (Section 3.6).

Before irradiation of samples containing FeCl$_3$, TiO$_2$ and TiO$_2$-RH/FeCl$_3$, no changes were seen in the concentrations of any sulfonamides (with the exception of SMX in the presence of TiO$_2$-P25). Most probably, they did not form stable, coordination compounds with Fe^{3+} ions, and the adsorption of sulfonamides on the particles of TiO$_2$ suspension was negligible.

An important parameter influencing the surface charge properties of TiO$_2$ particles is pH of the point of zero charge (pH$_{pzc}$).

$$Ti\text{-}OH_2^+ \underset{pH < pHpzc}{\overset{}{\rightleftharpoons}} Ti\text{-}OH \underset{pH > pHpzc}{\overset{}{\rightleftharpoons}} TiO^- \qquad (16)$$

In the case of TiO$_2$-RH, the value of pH$_{pzc}$ was 3.00 ± 0.05 [43] and was lower than pH of most sulfonamide solutions (Table 1). The TiO$_2$-RH surface was negatively charged at pH > 3.0, allowing sulfonamides to adsorb onto the catalyst. On the other hand, for TiO$_2$-P25, the value of pH$_{pzc}$ was 6.26 ± 0.05 [43] and was similar to pH of sulfonamide solutions. For this reason, most of the sulfonamides (with the exception of SMX) probably did not adsorb onto TiO$_2$-P25 surface.

Boreen et al. [40] have reported that the radical of the amide group does not have a large influence on the reaction rate of sulfonamides with HO• radical. This assumption was partially confirmed by the data of our studies. The dynamics of sulfonamide degradation depended mainly on the type of catalyst (with the exception of TiO$_2$-RH/FeCl$_3$). In all analysed cases, the initial reaction rate was higher for TiO$_2$-RH/FeCl$_3$, FeCl$_3$ or TiO$_2$-P25 and the lowest for TiO$_2$-RH (Table 1). Similarly to the case of SN, the sulfonamide degradation was a pseudo second-order process in the presence of TiO$_2$-RH/FeCl$_3$ and a pseudo first-order in the presence of other catalysts. Moreover, significant differences in the degradation rate for each sulfonamide were observed for TiO$_2$-RH/FeCl$_3$ (Table 1). In this case, a positive correlation was found between the concentration of the cationic form of sulfonamide (SH$_2^+$) and its determined degradation rate. The dependence of the r_o values on the concentration of the cationic form for a series of SA, SD and ST is described by the function: $y = 1.0356x - 0.0036$ ($R^2 = 0.9774$). Earlier, it was stated that the rate of sulfonamide degradation increased with decreasing pH of samples (Fig. 3).

In order to explain the mechanism of the initial step of the process catalysed by TiO$_2$-RH/FeCl$_3$, the following information should be taken into consideration:

- the rate of Fe^{3+} reduction is almost the same in the presence of TiO$_2$-RH/FeCl$_3$ as with FeCl$_3$ alone;
- SH$_2^+$ ions take an active part in the photocatalytic process;
- the photocatalytic process practically does not occur at pH 4–9.
- Based on this, we suppose that two parallel reactions occur;
- SH$_2^+$ cations are probably acceptors of electrons, forming a conduction band e$_{CB}^-$; simultaneously, these ions can undergo excitation:

$$TiO_2(h_{VB}^+, e_{CB}^-)(aq) + SH_2^+ \rightarrow HO^\bullet + SH^\bullet + H^+ \qquad (17)$$
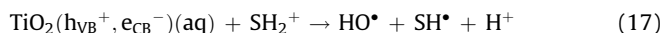
- HO• radicals are also generated in a reaction with the participation of Fe^{3+} or Fe(OH)$^{2+}$ (Eq. (2) or (6)).
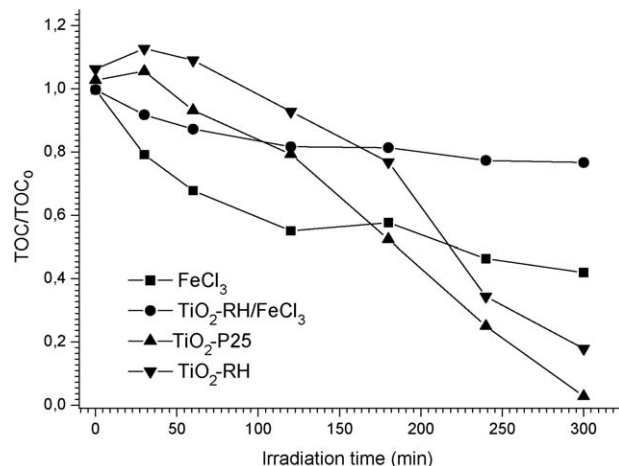
Fig. 6. Decrease of TOC value during UV-A irradiation of SN solution (0.1 mmol L^{-1}) with FeCl$_3$ (1.0 mmol L^{-1}), TiO$_2$-RH/FeCl$_3$ (2.5 g L^{-1}/1.0 mmol L^{-1}), TiO$_2$-P25 (2.5 g L^{-1}) or TiO$_2$-RH (2.5 g L^{-1}).

In the case of other catalysts (FeCl$_3$, TiO$_2$-P25 and TiO$_2$-RH), our results confirm the mechanisms described in the literature works cited in the introduction [18,22,23,25–30,38,39].

The optimum photocatalyst should be characterised by universality, i.e., high degradation efficiency of all compounds, high process rate and the possibility of obtaining a high degradation degree. In the presence of TiO$_2$-P25, the degree of sulfonamide degradation of >90% was obtained within the
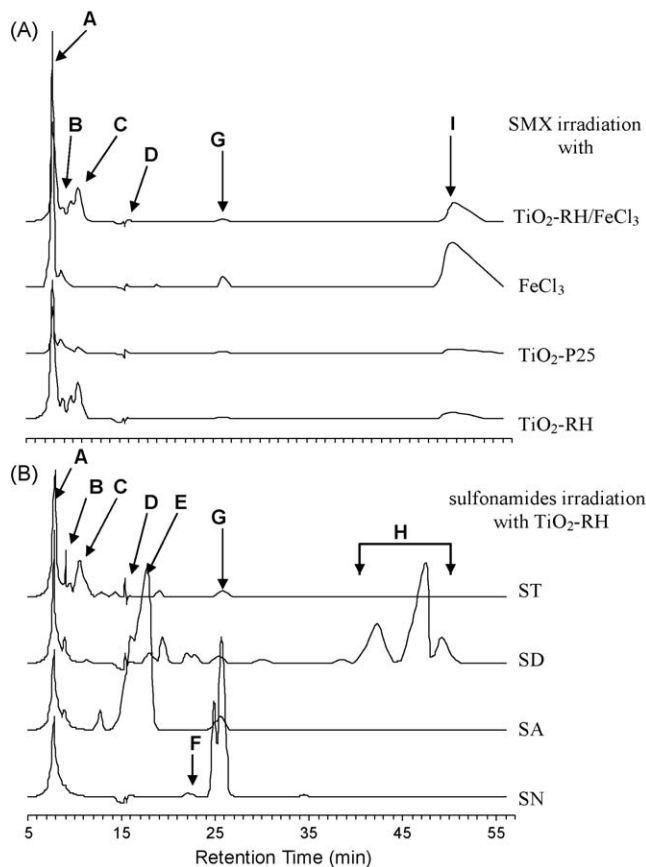

Fig. 7. Intermediates of the photocatalytic degradation of sulfonamides: (A) SMX (0.1 mmol L^{-1}) with TiO$_2$-RH/FeCl$_3$ (2.5 g L^{-1}/1.0 mmol L^{-1}), FeCl$_3$ (1.0 mmol L^{-1}), TiO$_2$-P25 (2.5 g L^{-1}) and TiO$_2$-RH (2.5 g L^{-1}), (B) other sulfonamides (0.1 mmol L^{-1}) with TiO$_2$-RH (2.5 g L^{-1}). The exampled chromatograms obtained after 120 min UV-A irradiation; recorded at 254 nm; mobile phase: CH$_3$CN:H$_2$O, 5:95.

shortest time. However, the highest initial rate was observed in processes catalysed by TiO_2-RH/$FeCl_3$ (Table 1). Moreover, $FeCl_3$ by itself possessed high photocatalytic activity. Since its application is the cheapest as well as the least troublesome technologically, this compound was selected as the optimum photocatalyst for the degradation process of sulfonamides.

3.9. Photocatalytic mineralisation of sulfonamides

The degree of TOC removal in samples was recognised as the measure of mineralisation of sulfonamides during irradiation of their solutions. Fig. 6 shows the dynamics of TOC changes during illumination of SN solutions (0.1 mmol L^{-1}) with selected catalysts: $FeCl_3$ (1.0 mmol L^{-1}), TiO_2-RH/$FeCl_3$ (2.5 g L^{-1}/ 1.0 mmol L^{-1}), TiO_2-P25 (2.5 g L^{-1}) and TiO_2-RH (2.5 g L^{-1}). The degrees of TOC removal of all investigated sulfonamide solutions obtained after 300 min of exposure to UV-A radiation are presented in Table 1.

In accordance with our assumption, the mineralisation of selected sulfonamides required considerably longer irradiation time than their degradation. A significant decrease in TOC was observed during 30–300 min irradiation of samples containing TiO_2-P25 and TiO_2-RH. In the case of sulfonamide solutions with $FeCl_3$ and TiO_2-RH/$FeCl_3$, a decrease in TOC occurred after 0–120 min of irradiation and was 43 and 16%, respectively (Fig. 6). Moreover, in these samples, the TOC removal was negligible during 120–300 min of irradiation. Most probably, it is caused by the

almost complete reduction of Fe^{3+} ions described earlier and a low rate of Fe^{2+} oxidation. Due to the aforementioned reasons, the achievement of practically 100% mineralisation is probably possible with only TiO_2-P25 and TiO_2-RH suspensions but may require long illumination times, exceeding 300 min.

From the practical point of view, the achievement of complete mineralisation of samples during the photocatalytic process is not necessary. The results our preliminary studies imply that intermediates of sulfonamide degradation undergo biodegradation [17].

3.10. Chemical mechanism of sulfonamide photodegradation

Boreen et al. [40] have performed a review of available data in the literature regarding the pathways of sulfonamide degradation. In the theoretical part, as the organic intermediates of sulfonamide decomposition, the authors specify mainly sulfanilic acid, as well as sulfanilamide, aniline and benzenesulfonic acid. However, during investigation of a reaction between $HO^\bullet$ radicals and sulfa drugs containing five-membered heterocyclic groups, they identified only the fission products after cleavage of the radical of the amide group. As intermediates of photocatalytic degradation of sulfonylurea herbicides, Vuilliet et al. [26] have specified hydroquinone, benzoquinone, phenols, malonic acid, oxalic acid, formic acid and products of elimination of the radical of the amide group and its degradation. Similarly, Rafqah et al. [27], Hu et al. [29] and Sukul and Spiteller [44] have reported that an attack by the $HO^\bullet$

Table 2
Intermediate products of photocatalytic degradation of sulfonamides (presented in Fig. 7).

Symbol in Fig. 7	Compounds	Samples		Theoretical fragmentation of compounds	Standard
		t_R (min)	MS-spectra[a]		t_R (min)
A	Sulfanilic acid	7.40	173 (40), 156 (60), 108 (90), 93 (80), 92 (100)	$m/z = [M]$ $m/z = [M]-OH$ $m/z = [M]-SO_2H$ $m/z = [M]-SO_2-NH_2$ $m/z = [M]-SO_3H$	7.46
B	Oxalate acid[b]	7.77–8.09	–	–	7.80
C	Benzenesulfonic acid	9.88–10.26	158 (30), 141 (30), 94 (80), 77 (100)	$m/z = [M]$ $m/z = [M]-OH$ $m/z = [M]-SO_2$ $m/z = [M]-SO_3H$	9.82
D	Acetic acid[b]	15.39–16.00	–	–	15.50
E	Sulfacetamide	17.87	172 (30), 156 (50), 108 (70), 93 (100), 92 (60)	$m/z = [M]-R$ $m/z = [M]-NHR$ $m/z = [M]-SONHR$ $m/z = [M]-SON_2H_3R$ $m/z = [M]-SO_2NHR$	17.71
F	Benzenesulfonamide	22.21–22.76	157 (20), 141 (30), 93 (40), 77 (100)	$m/z = [M]$ $m/z = [M]-NH_2$ $m/z = [M]-SO_2$ $m/z = [M]-SO_2NH_2$	22.19
G	Sulfanilamide	24.83–25.84	172 (30), 156 (60), 108 (90), 92 (100)	$m/z = [M]$ $m/z = [M]-NH_2$ $m/z = [M]-SONH_2$ $m/z = [M]-SO_2NH_2$	25.12
H	Sulfadiazine	47.49–49.23	186 (70), 185 (100), 93 (60), 92 (70)	$m/z = [M]-SO_2$ $m/z = [M]-SO_2H$ $m/z = NHR$ $m/z = [M]-SO_2NHR$	47.60
I	Sulfamethoxazole	50.50–50.83	253 (20), 156 (50), 108 (50), 92 (100)	$m/z = [M]$ $m/z = [M]-NHR$ $m/z = [M]-SONHR$ $m/z = [M]-SO_2NHR$	51.05

[a] Excited by EI method, recorded at $m/z > 76$ or 91.
[b] Compounds were identified only by comparison of the retention times with a pure standard, on chromatograms recorded at 220 and 254 nm.

radical led to the elimination of the amide group from sulfonamide. Inorganic products such as CO_3^{2-} (CO_2), SO_4^{2-}, NO_3^- and NH_4^+ ions were also reported [18,26,29,40]. Moreover, in the case of irradiation of sulfonamide solutions by high-energy radiation, e.g., UV-C, the formation of azo- and azoxydisulfonamides was observed [18,42].

The aim of our study was the determination and comparison of the mechanisms of photocatalytic degradation of sulfonamides depending on the type of catalyst used. Therefore, no identification was made of products of their elimination and the decomposition of amide residues. The intermediates obtained as a result of the photocatalytic processes carried out in the presence of the investigated catalysts were also compared. Fig. 7A presents chromatogram examples of degradation products of SMX (0.1 mmol L^{-1}) obtained after 120 min of irradiation of solutions containing different photocatalysts (TiO_2-P25, TiO_2-RH, TiO_2-RH/$FeCl_3$ or $FeCl_3$). Chromatograms containing degradation products of SN, SA, SD and ST in the presence of TiO_2-RH (after 120 min of irradiation) are shown in Fig. 7B.

An HPLC/MS-EI method was applied, using standards of the compounds (Section 2.4). The retention times (t_R) of peaks and the mass spectra of identified substances are shown in Table 2. Moreover, after illumination, the inorganic ions and phenols were detected in solutions using colorimetric methods. It was confirmed that in sulfonamide solutions after exposure to UV-A radiation, NO_3^- ions (method with sulfasalicylic acid), NH_4^+ ions (method with Nessler's reagent), o-phenols and/or m-phenols (method with 4-aminoantypyrine) were present. In earlier studies, it was confirmed that HO• radicals were generated in samples containing TiO_2-P25, TiO_2-RH, TiO_2-RH/$FeCl_3$ or $FeCl_3$ after illumination with UV-A radiation (Section 3.2).

It was stated that the same intermediates were identified independently of the type of catalyst. However, their concentrations (the peak intensities) were different: the highest in the presence of TiO_2-RH/$FeCl_3$ and TiO_2-RH in a basic medium and the lowest for TiO_2-P25 at pH 4–6 (Fig. 7A). These results are in correlation with the degree of mineralisation of samples (Section 3.5), implying that this stage of the process most probably does not show qualitative differences with the use of the different photocatalysts.

Similar observations were obtained during analysis of chromatograms of the other sulfonamides. The highest concentrations of intermediates and the lowest of mineralisation degree were in the case of SD (Fig. 7B). None of analysed samples contained hydroquinone, benzoquinone and aniline. From the practical point of view, it is important to note that the particularly high concentration of sulfanilic acid occurred at the beginning of irradiation in all analysed sulfonamide samples. During degradation of SN, the maximum concentration of sulfanilic acid in the range of 0.005–0.01 mmol L^{-1} was achieved after about 25, 30 and 100 min of UV-A irradiation in the presence of $FeCl_3$, TiO_2-RH/$FeCl_3$ and TiO_2-RH, respectively (in contrast, in the case of TiO_2-P25, the determined concentration of sulfanilic acid was significantly lower). In samples in which 50% of SN underwent degradation in the presence of $FeCl_3$, TiO_2-RH/$FeCl_3$, and TiO_2-RH and TiO_2-P25, the concentrations of sulfanilic acid were 0.004, 0.007, 0.003 and 0.001 mmol L^{-1}, respectively. The concentrations of other identified organic compounds were clearly lower. Similar results were observed during the comparison of chromatograms obtained using the other mobile phase ($CH_3CN:H_2O$, 1:1).

Based on the above-described results, we suppose that the process of photocatalytic degradation of sulfonamides can be divided into the following stages (Fig. 8):
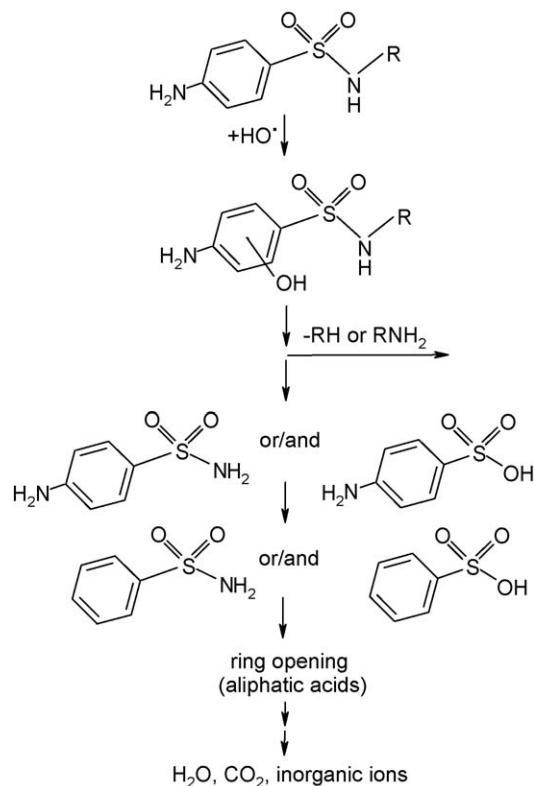
- hydroxylation of the aromatic ring,

Fig. 8. Proposed pathways of the photocatalytic degradation of sulfamides.

- elimination of the amide group and/or the radical of the amide group,
- elimination or substitution of the amide and the sulfonyl group,
- opening of the aromatic ring, and
- oxidation of aliphatic acids.

4. Conclusions

All investigated sulfonamides undergo photocatalytic degradation in processes conducted in the presence of Fe^{3+} salts (homogeneous process) and in the presence of TiO_2 and TiO_2-RH/$FeCl_3$ (heterogeneous process). Among the Fe^{3+} salts used, the highest catalytic activity was provided by $FeCl_3$ and $Fe(NO_3)_3$, while among the heterogeneous catalysts, TiO_2-P25 and TiO_2-RH/$FeCl_3$ were most active. In processes with Fe^{2+} salts, the photocatalytic degradation of sulfonamides proceeds at a significantly slower rate. The optimum photocatalyst for degradation of sulfonamides was $FeCl_3$ due to its high catalytic activity, low cost, non-toxicity and simplicity of the technological process. The photocatalytic process carried out in the presence of $FeCl_3$ occurred only in a narrow pH range, with a maximal rate at about pH 3. It was found that the initial concentrations of sulfonamide and $FeCl_3$ had a significant influence on the photocatalytic reaction rate, which is likely connected with the effective use of radiant flux.

The photocatalytic process was initiated by hydroxyl radicals. However, in the presence of TiO_2-RH/$FeCl_3$, the reduction of the cationic form of sulfonamide by excited electrons from the conduction band of TiO_2 is also possible.

The pathways of the photocatalytic degradation of all investigated sulfonamides are likely the same, independent from used photocatalysts.

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